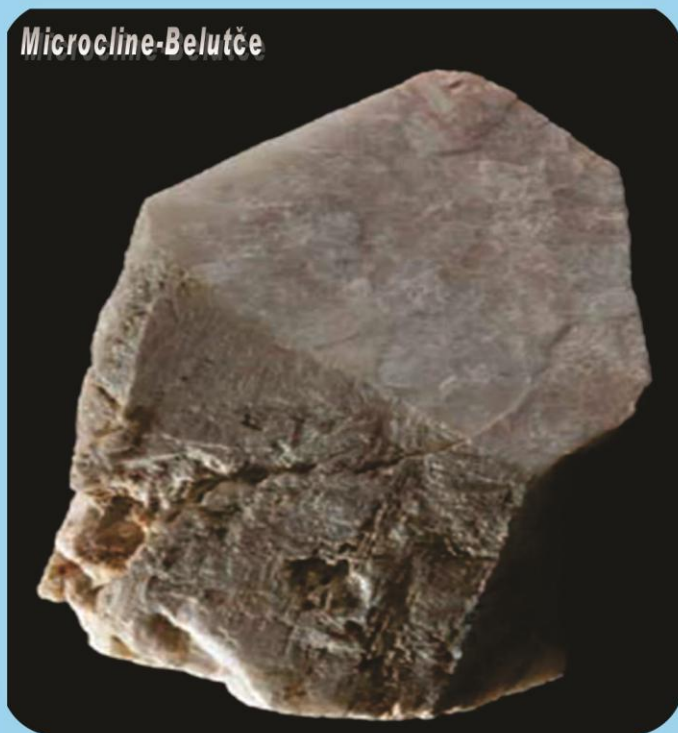


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HYDROCHEMICAL DATA FOR THE GROUND WATERS IN THE BITOLA'S PART OF THE PELAGONIA VALLEY, REPUBLIC OF MACEDONIA

Vojo Mirčovski, Blažo Boev, Zlatko Efremoski, Ajka Šorša, Đorđi Dimov

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A b s t r a c t: For determination of some hydrochemical data in the ground waters of the Bitola part of the Pelagonia valley, are taken single samples from 19 wells. Specified values for pH indicate that the waters belong to the group of slightly alkaline ground water ($\text{pH} = 7.2 - 8.9$). Following to the classification of Alekin the majority of tested water according the content of the anion fall into hydrocarbonate class, calcite group and a smaller number in the chloride and sulfate class, sodium and magnesium group. Increased values of TDS, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- and NH_4^+ occurs in the ground water from deeper artesian and subartesian wells, as a result of the longer retention time of water in the underground and its interaction with the geological environment. Ground water from the shallow wells occurs the increasing content of PO_4^{3-} and NO_3^- which indicates water pollution from fertilization of the cultivated areas, livestock farms as well as communal waste water. Knowing the hydrochemical feature of the ground water from the research area is from particular importance, because the water from these wells is used by the inhabitants of the region as industrial water, water for irrigation, packaging of mineral water and the exploitation of CO_2 .

Key words: ground water; wells; Pelagonia valley; cations; anions; hydrochemical characteristics

INTRODUCTION

In recent decades, the quality of the ground water as a result of the anthropogenic activities significantly deteriorated, so it is necessary to make efforts to preserve and enhance the quality of the ground water (Mirčovski et al., 2014). In many parts of the country, the use of the ground water as drinking water is unquantifiable because of their contamination by various human activities. In the Bitola part of the Pelagonia valley ground water

used by the population as technical water, water for irrigation of agricultural areas, and packaging of the mineral water. The Pelagonia valley is located in the southwestern part of the Republic of Macedonia (Fig. 1). The valley is bounded to the west with the mountains Baba, Plakenska and Bušava, Dautica from north, and the Babuna and Selečka mountains from the east side.

GEOLOGICAL FEATURES

According tectonic regionalization of the Republic of Macedonia, the Pelagonia valley belongs to the Pelagonia horst anticlinorium (Arsovski, 1997). Pelagonia valley presents neotectonic basin structure whose formation began at the end of Middle Miocene (Dumurdžanov et al., 2002).

The Pelagonia valley is built from Neogene lake sediments represented by sandy silt stones, sandy clay, clean silt stones and clays which are dominant. In profile less prevalent siltstones sand

and gravel, and clean layers of sand and gravel. Above the lake sediments can be found Quaternary alluvial sediments represented by alluvial lake sediments, both them more prevalent coarse sandy gravely fraction and marsh sediments. Following end of the basin, Quaternary sediments are represented by proluvial and diluvial deposits built from roughly clastic sediment of silty-clay, sands and gravels (with the local occurrence of coarse gravel).

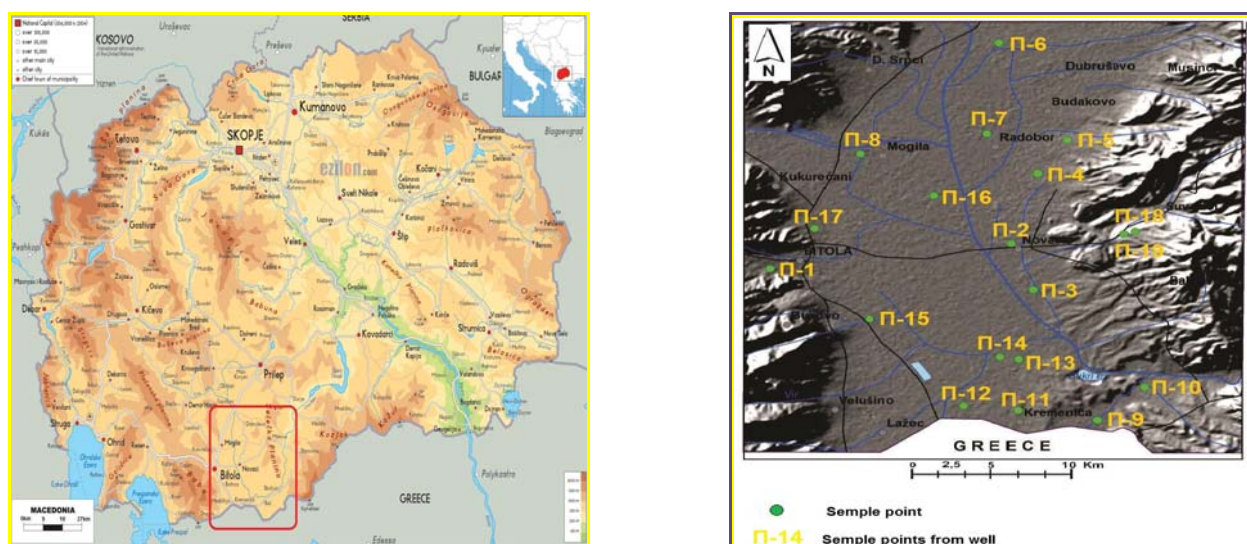


Fig. 1. Geographical location of the research site and location of the wells from which the samples were taken

The wider region of the the research area is basically built from Precambrian and Paleozoic metamorphic rocks that have been developed by the peripheral mountains and at the base of the Neogene lake sediments.

Precambrian metamorphic rocks represent a higher-grade rocks usually presented with the vari-

ed gneisses, micaschist, granodiorites, granites, calcite marble and dolomitic marbles.

Paleozoic rocks are represented by quartz-sericite and graphite shale, metasandstone and quartzite and epidote-chlorite amphibole schists (Dumurdžanov, et al., 1979).

HYDROGEOLOGIC FEATURES

Rock masses in the Bitola part of the Pelagonia valley toward their hydrogeological function are separate as: hydrogeological collectors, hydrogeological conductors, hydrogeological complexes and hydrogeological insulators.

On the basis of the geological structure and structural type of porosity within the rocks in the wider region of the Bitola field include the following types of aquifers: aquifers with intergranular porosity, aquifers with fissure porosity and conditional arid areas (Gjuzelkovski 1997; Karajovanović, Ivanovski, 1972).

As hydrogeological collectors and conductors are separated rocks with intergranular porosity. In the group of hydrogeological complexes are separate Neogene sediments, and in the group of hydrogeological insulators allocated swampy sediments, clays and siltstones within the Neogene complex as well as poorly cracked solid rock masses.

According hydrodynamic features that govern within the aquifer environments include the following types of aquifers: fraetic type of aquifers (aquifers with free level of ground water) and artesian and subartesian aquifers type (aquifers with pressure level ground water).

METHODS AND MATERIALS

In order to be analyzed some hydrochemical characteristics of the ground water from the Bitola part of the Pelagonia valley are taken samples from 19 wells. The locations of the wells that have taken samples are shown in Fig. 1, and the coordinates and their technical characteristics in Table 1.

Taking samples is made once in the time continuum of the day 27. 8. 2013. Values of the pH

were determined with the field digital pH-meter, while cations are determined by AES-ICP, Libery 110, Varian. For the determination of the anions are used standard EPA methods (gravimetric – TDS, volumetric – Cl^- , spectrophotometric – NO_3^- , NO_2^- , NH_4^+ and turbidimetric – SO_4^{2-} with the spectrophotometer 6715 UV / VIS, Jenway) (Broun et al., 1974; Harilal et al., 2004).

Table 1

Obtained results from hydrochemical analysis from ground water in the Bitola part of the Pelagonia valley

PARAMETAR			Ca	Mg	Na	K	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	PO ₄ ³⁻	NH ₄ ⁺	NO ₂ ⁻	TDS VK	pH
Sample point	Location, depth and capacity of the wells	COORDINATES		MAXIMUM PERMITTED CONTENTS (MPC) (mg/l)											
		Y	X	200.0	50.0	200.0	12.0	250.0	250.0	50.0	6.7	0.1	0.03	2000	
P 1	Bitola hospital; 80 m; 1,3 l/s	7 527 315 4 542 328		24.5	12.2	23.5	2.8	93.6	36.7	17.1	2.0	0.15	<0,01	268	8.1
P 2	v. Novaci; 8 m; 0.5 l/s	7 538 800 4 544 375		101.6	28.9	49.0	7.9	99.7	111.0	296	33	0.50	0.029	<0,01	699 8.3
P 3	v. Ribarci; 50 m; 5 l/s	7 539 890 4 540 806		134.9	74.3	135	7.4	305.0	495	27.6	9.4	0.19	<0,02	<0,01	874 8.1
P 4	v. Aglarci; 70 m; 3 l/s	7 540 040 4 549 928		65.3	33.8	6.3	4.0	151.0	111.0	43.6	23	0.17	<0,02	<0,01	451 8.7
P 5	v. Dedebalci; 85 m; 3.5	7 541 440 4 552 550		58.4	20.9	21.1	3.0	90.6	66.0	37.6	36	0.11	<0,02	<0,01	356 8.6
P 6	v. Nošpal; 7 m; 0.5 l/s	7 538 162 4 560 188		72.2	24.9	118	195.7	211.4	253	135	167	3.0	0.069	<0,01	1016 8.8
P 7	v. Radobor; 30 m; 3.5 l/s	7 537 606 4 553 034		45.2	13.5	27.6	2.4	111.7	59.7	21.1	5.9	0.18	0.030	<0,01	300 8.7
P 8	v. Mogila; 30 m; 3 l/s	7 531 577 4 551 402		80.9	33.8	33.1	1.9	151.0	132.0	47.2	23	0.22	0.043	0.014	481 8.8
P 9	v. Germijan; 120 m; 20 l/s	7 543 012 4 530 524		299.5	196.3	1215	112.2	1797	1702	35.4	0.73	0.052	6.2	<0,01	4399 7.6
P 10	v. Bač; 300 m; 50 l/s	7 545 262 4 533 125		272.3	141.2	1563	109.1	1709	2813	302	1.3	<0,015	5.9	<0,01	5431 8.9
P 11	v. Kremenica; 120 m; 5 l/s	7 539 213 4 531 294		186.9	69.0	43.0	10.2	673.5	72.3	35.2	<0,1	1.1	0.73	<0,01	1293 7.2
P 12	v. Medžitlija; 120 m; 4 l/s	7 536 633 4 531 630		96.6	40.5	69.4	9.8	289.9	41.9	197	0.56	0.13	0.47	<0,01	872 8.2
P 13	v. Egri 1; 120 m; 5 l/s	7 539 206 4 535 297		217.1	73.3	114.8	15.2	649.3	74.4	338	0.18	0.45	0.54	<0,01	1678 7.6
P 14	v. Egri 2; 300 m; 80 l/s	7 538 344 4 535 479		273.5	384.0	50.5	54.4	1891	633	219	0.22	0.036	2.2	<0,01	4452 8.5
P 15	v. Kravari; 45 m; 4.5 l/s	7 532 087 4 538 456		43.2	24.1	20.7	3.4	111.7	73.3	43.8	6.3	0.41	0.087	<0,01	360 8.2
P 16	v. Trn; 300 m; 50 l/s	7 535 136 4 548 150		253.9	379.5	1185	67.9	2295	2267	4.4	3.8	<0,015	11	<0,01	6903 8.2
P 17	v. Orizari; 9,5 m; 0.3 l/s	7 529 441 4 545 530		52.6	16.5	28.0	2.2	120.8	72.3	31.9	39	0.52	0.056	<0,01	363 8.7
P 18	REK 1 B-19; 66 m	7 544 739 4 545 344		74.7	38.4	37.8	6.1	132.9	68.1	201	0.42	4.9	0.49	0.035	636 7.7
P 19	REK 2 B-14; 125 m	7 544 210 4 545 168		78.1	33.3	51.3	7.0	187.2	95.3	108	0.86	2.5	0.50	<0,01	540 8.4

RESULTS AND DISCUSSION

Obtained hydrochemical data are shown in Table 1, a their spatial distribution in Figs. 2–13. The measured data are compared with the Macedonian standard for drinking water which is made by criteria which apply to the European standards (MDK – OGRM, No. 57, 2004; (WSR, OGRM, No. 46, 2008).

pH is an important environmental factor which provides information on many types of geo-

chemical balances (Shyamala et al., 2008). pH affects not only the reaction with CO₂, but also the solubility of the organic and inorganic substances in the water. Any change of pH in water is accompanied by changes in other physical-chemical parameters. Normal range of values for surface and ground water is 6.5 to 8.5. Water with lower values for pH of 6.5 have weak acidic character and generally is soft and corrosive (Fig. 2).

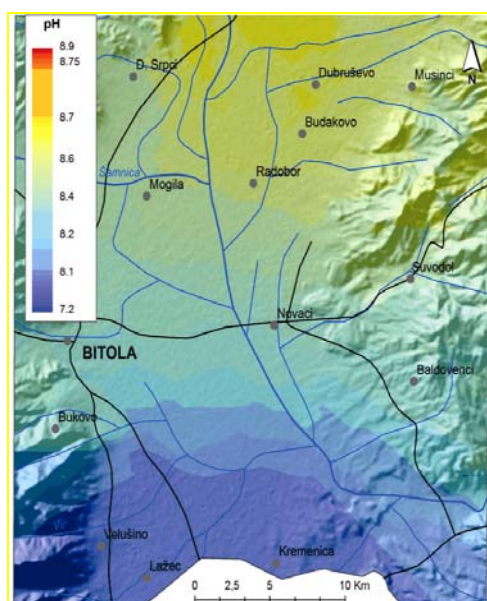


Fig. 2. Spatial distribution of pH

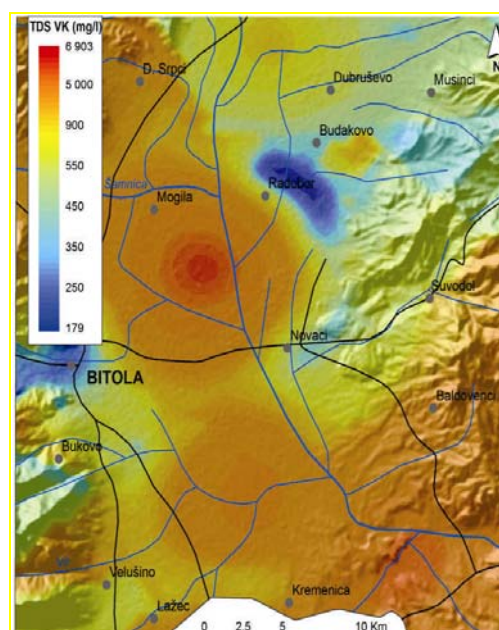


Fig. 3. Spatial distribution of TDS/mg l⁻¹

Those may results with metallic or sour taste and distinctive "blue-green" coloration. Those water may contain higher concentrations of metals, for example, Fe, Mn, Cu, Pb, Zn, Pb. Measured values of pH for ground waters are in the limits of 7.2 (P-11, village of Kremenica, well with a depth of 120 m, used for the production of mineral water) and 8.9 (P-10, village of Bač, well with a depth of 300 m, factory "BUSEMAK" for production of CO₂). From 19 examined samples the measured values of 7 of them exceed the allowed value, while other samples are within the permissible values according to the rulebook for drinking water (6.5 to 8.5).

According to the values of pH, tested samples of ground water belong to the group of slightly alkaline ground water.

TDS is used for estimation of total dissolved salts in water (Purandara et al., 2003), which may have an impact on the taste and suitability of water for various purposes. The measured values for TDS in the tested waters ranging from a minimum value of 268 mg/l in (P-1, Bitola city hospital, well with a depth of 80 m) to the maximum value of 6903 mg/l in (P-16, village of Trn, well with a depth of 300 m, factory for produce CO₂ "GEO-GAS"). It should be noted that the wells P-9, (v. Germijan), P-10 (v. Bač), P-14 (v. Egri) and P-16 (v. Trn) are used for exploitation of CO₂ and have higher values of TDS that exceed the maximum allowable concentration for drinking waters. All the rest do not exceed the recommended maximum allowable concentration values for drinking water, 2000 mg/. (Fig. 3).

Can be said that the value of total dissolved salts in ground water increases with increasing depth of the wells, i.e. it is higher in the water coming from artesian and subartesian wells.

Based on the total mineralization, ground waters belong to the slightly mineral waters (<1 g/l), mineralized waters (> 1 g/l) and in the group of waters with increased mineralization (15 g/l).

Increased concentrations of total dissolved ionic substances are the result of the geology of the terrain and longer residence time of water in the underground.

According to WHO (World Health Organization), waters containing more than 500 mg/l TDS are not recommended for drinking and can lead to some diseases due to excess of dissolved salts. (Ballester and Sunyer, 2000).

Calcium (Ca²⁺) and magnesium (Mg²⁺). The content of Ca²⁺ and Mg²⁺ determines the water hardness, which is an important parameter for reducing the toxic effects of some of the elements. In five of the tested samples specific content of Ca²⁺ exceeds the maximum permitted content (MPC) values for drinking water (Ca 200 mg/l), and in 7 of the tested samples specific content of Mg²⁺ is higher than (50 mg/l) allowed for drinking water. On average the number of tested samples of water in which the measured concentration of magnesium is higher than 50 mg/l, value of the MPC for drinking water, compared to the calcium (Figs.4 and 5). High values for total hardness of the tested results are mainly due to dissolution of carbonate rocks.

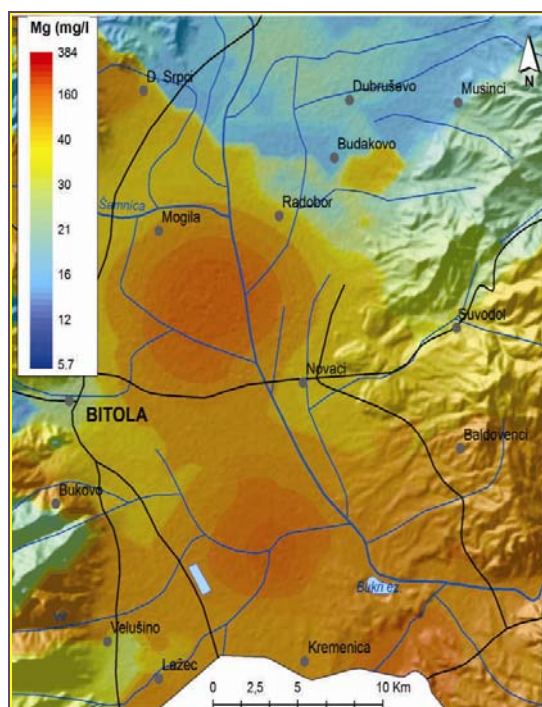


Fig. 4. Spatial distribution of $\text{Ca}^{2+}/\text{mg l}^{-1}$

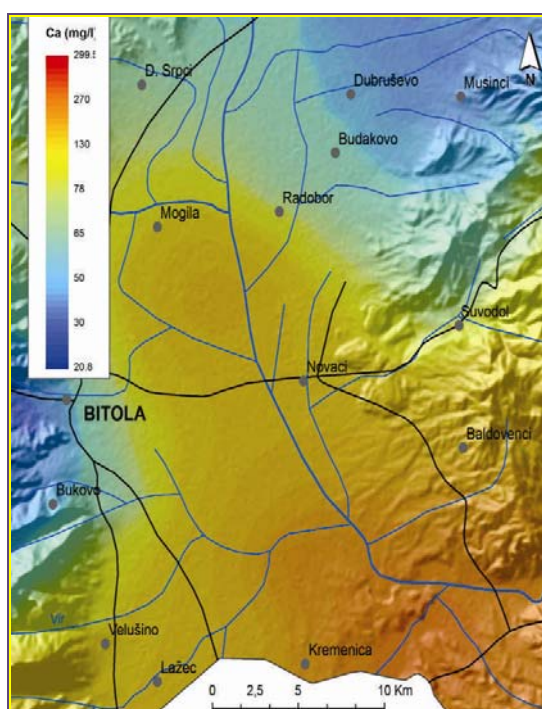


Fig. 5. Spatial distribution of $\text{Mg}^{2+}/\text{mg l}^{-1}$

Sodium (Na^+). Range of specific concentrations of sodium is the minimum value (6.3 mg/l) in P-4 (village of Aglarci, drilling well with a depth of 70 m) up to maximum (1563 mg/l) in P-10 (village of Bač drilling well with a depth of 300 m, plant "BUSEMAK" used it for the production of CO_2). Only in three of the tested samples of water,

sodium content is higher than the maximum allowable concentration for drinking water (200 mg/l) (Fig. 6).

The content of Na^+ also increases which the water coming from deeper artesian and subartesian wells.

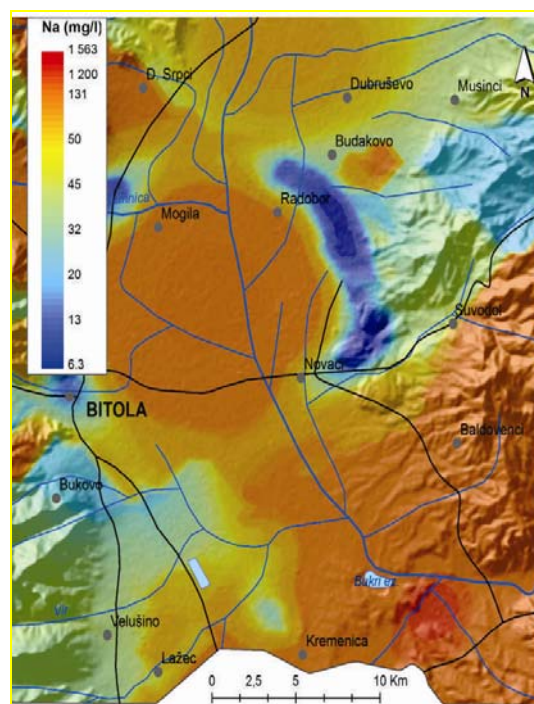


Fig. 6. Spatial distribution of $\text{Na}^+/\text{mg l}^{-1}$

Potassium (K^+). Range of specific concentration of potassium is very wide (Fig. 7), the minimum value of 1.9 mg/l in P-8 (v. Mogila, drilling well with a depth of 30 m), up to maximum of 195.7 mg/l in P-6 (v. Nošpal brickworks well with a depth of 7 m). In the tested samples content of potassium is higher than the maximum allowable concentration for drinking water (12 mg/l), in 6 samples.

Increasing the contents of K^+ in the ground water present in the deeper artesian and subartesian wells, except well P-6.

HCO_3^- . Values for concentration of alkalinity in water expressed as hydrogen carbonate anions indicate the nature of the salts present in the water. The reason for the alkalinity of the water is dissolution of minerals from the soil into the water. Different ions have their own part of alkalinity, such as, hydrogen carbonates, hydroxides, phosphates, borates and organic acids. These factors are characteristic of water sources and natural processes occurring (Sharma, 2004).

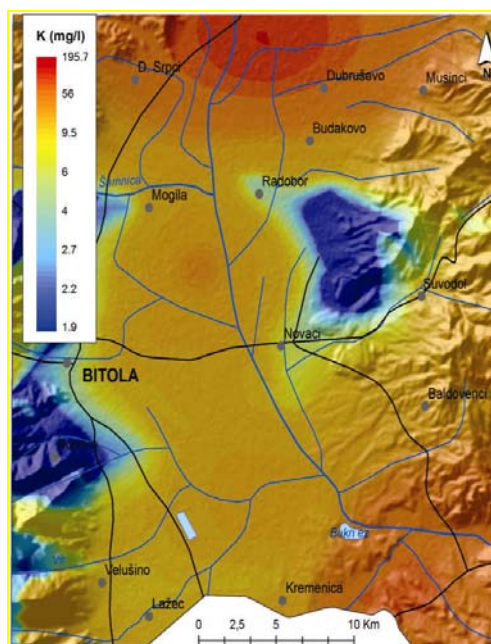


Fig. 7. Spatial distribution of K^+ /mg l^{-1}

The range of specific concentration of hydrogen carbonates identified as alkalinity is the minimum value of 90.6 mg/l in P-5 (village of Dede-balci) drilling well with a depth of 85 m, used as industrial water for domestic use and irrigation of grass surfaces, up to maximum of 2295 mg/l at P-16 (village of Trn, drilling well with a depth of 300 m, plant "GEOGAS", uses it for the production of CO_2), (Fig. 8).

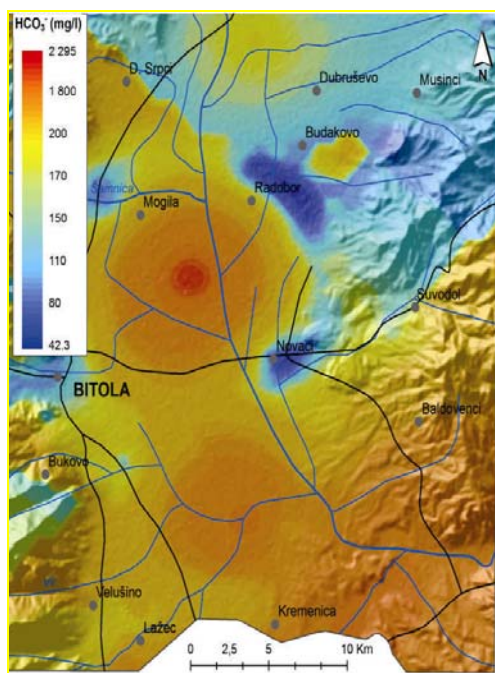


Fig. 8. Spatial distribution of HCO_3^- /mg l^{-1}

Chloride (Cl^-) Chloride is usually encountered as $NaCl$, $CaCl_2$ and $MgCl_2$ in a great range of concentrations in natural waters. They can also be contaminants of underground waters whose source can be sewage waters and waste (Shaikh and Mandre, 2002).

Chloride (Fig. 9) is determined in a concentration range of 36.7 mg/l in P-1 (Bitola City Hospital), drilling well with a depth of 80 m up to 2813 mg/l in P-10 (v. Bač) drilling with depth of 300 m, used of the plant "BUSEMAK" for producing of CO_2 .

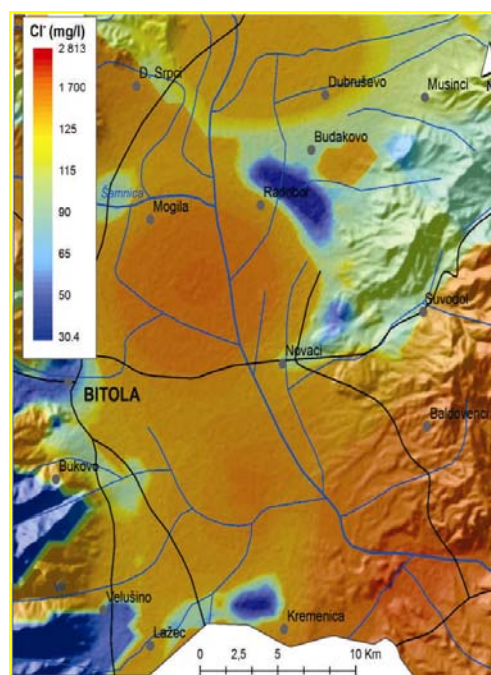


Fig. 9. Spatial distribution of Cl^- /mg l^{-1}

Maximum permitted concentration (MPC) for chloride in drinking water, according to the rule-book for security of drinking water of Macedonia, is 250 mg/l, but there are literature data on tolerance of chloride in concentrations of 200–1000 mg/l. According to the content of the specified chlorides, in 6 of the tested samples content higher than 250 mg/l is determined.

In the chlorides it is also perceived an increase in the content of Cl^- in ground water that originate from deeper artesian and subartesian wells.

Sulfates (SO_4^{2-}) Sodium sulfate and magnesium sulfate have a laxative effect on people, and also are associated with some respiratory diseases. Sulphates may be an indicator of water pollution by mine waste waters. Concentration range of sul-

phates in tested samples (Fig. 10) is minimal (4,4 mg/l) in P-16 (v. Trn) drilling well with a depth of 300 m plant "GEOGAS" for production of CO₂, up to 338 mg/l in P-13 (v. Egri), village source with mineral water, drilling well with a depth of 120 m. The concentration of sulphate anions in 3 water samples exceeds maximum permitted contents (MPC) for drinking water, so the water is undrinkable.

In the content of SO₄²⁻ is not noticed any pattern in terms of appearance.

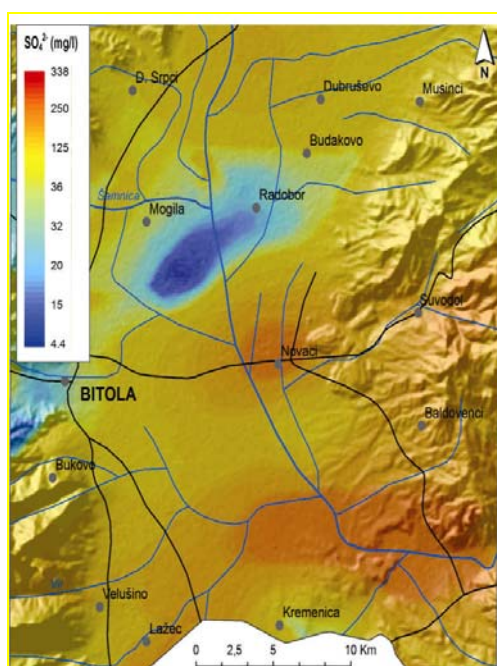


Fig. 10. Spatial distribution of SO₄²⁻/mg l⁻¹

PO₄³⁻. The results of the measurements of the concentration of dissolved phosphorus (expressed in the form of phosphates) are ranging from the minimum (<0.015 mg/3) in P-10 (village of Bač), drilling well with depth of 300 m) plant "BUSEMAK" for producing of CO₂, and (P-16) village Trn drilling well with a depth of 300 m, plant "GEOGAS" for production of CO₂. The extremely high value (4.9 mg/l) is detected in P-18, Mining and Energy Combine (REK-Bitola) and in P-19 drilling well, deep 66 m used for drainage of surface mine (Fig. 11). None of the tested samples did not exceeds the permitted concession of phosphates than the maximum allowable concentration (MAC) to drinking water (6.7 mg/l). Higher values (MPC) is unusual for a natural presence of phosphate in natural waters, their increased concentration indicates possible contamination of water with fertilizers and pesticides in the study area.

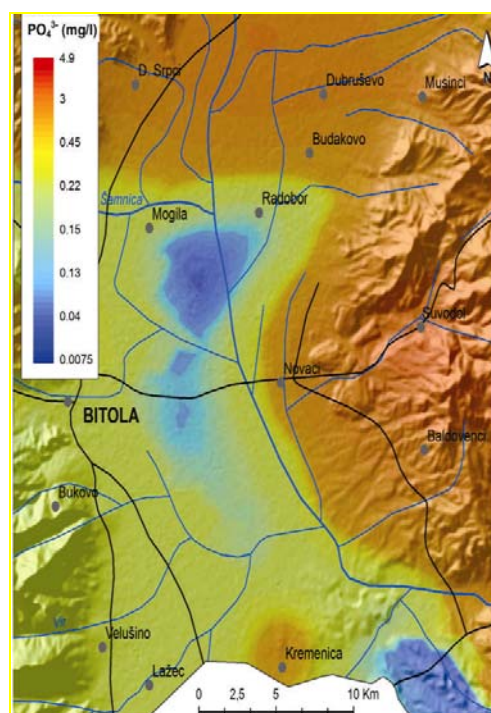


Fig. 11. Spatial distribution of PO₄³⁻/mg l⁻¹

Nitrates (NO₃⁻). Concentration of nitrates in the water indicates biological contamination (Manassaram et al., 2006). The range of specific concentration of nitrate anions (Fig. 12) is the minimum value of <0.1 mg/l in P-11 (v. Kremenica), drilling well with a depth of 120 m which is used for production of mineral water, to maximum of 167 mg/l in P-6 (v. Nošpal) brick-works well with a depth of 7 m used by locals for technical needs.

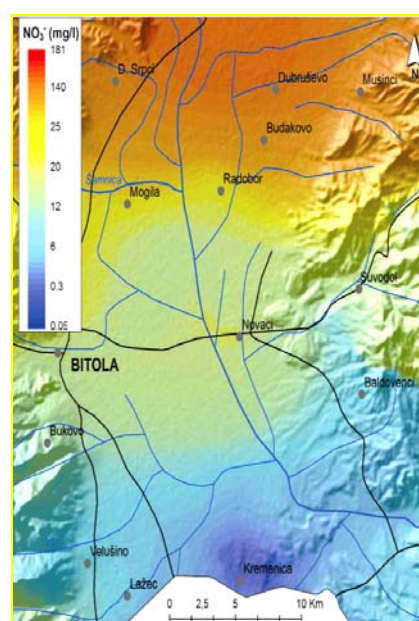


Fig. 12. Spatial distribution of NO₃⁻/mg l⁻¹

In one of the 19 surveyed samples measured values for nitrate anions exceed the allowed value of 50 mg/l according to the MPC. Increased content of nitrate occurs in underground waters originate from shallow wells.

Obtained values of the tested results indicate greater load of underground waters with organic substances as a result of pollution from municipal waste water, waste water from farms or pollution by fertilizers that contain nitrate anions.

Nitrites (NO_2^-). Consuming water that contains nitrate in high concentration presents a health risk due to the possible transformation of nitrate to nitrite in the digestive system. Nitrite oxidizes the iron in hemoglobin in red blood cells to methemoglobin which also leads to reduction in the ability of hemoglobin to transport the necessary oxygen to the cells in the organism. Nitrite ions of 19 examined samples of water higher than the upper limit for the maximum allowed concentration for drinking water (0,01 mg/l), are detected in two samples: in P-8 (v. Mogila) drilling well with a depth of 30 m which is used for irrigation of agricultural areas and in P-18 (Mining and Energy Combine – REK-Bitola B-19/ drilling well with a depth of 66 m, which is used for drainage of surface mine. Nitrite is an intermediate product in the continuing transformation of nitrogen in soils, denitrification (anaerobic) – nitrification (aerobic). Because of the low stability in acidic soil conditions, nitrite may be important components in the process loss of nitrogen from the soil. Soil organic substances and inorganic phases had a stimulating effect on the decomposition of nitrite in acid conditions (Van Cleemput, 1984). Also, the process of transformation of nitrogen in soil presence assets bacteria is very important for which optimal biological activity the environment's pH should be 6–7.5. In the content of nitrite is not detectable some pattern.

The concentration of nitrogen forms varies during rainy seasons due to intensive washing of the soil and low temperature operations of block nitrifying bacteria.

Ammonium ion (NH_4^+) is an indicator of the dynamic self-cleaning of contaminated water.

Increased content of ammonium ions occurs in ground water that originate from deeper artesian and sub artesian wells.

Ammonium ions are detected in nine samples tested water (Fig. 13), concentration of ammonium ions is higher than the maximum permitted (MPC) value of the drinking water (0.1 mg/l).

According to the classification of Alekin the greatest number of examined water by anion are classified into hydro-chloride class, and according to cations in calcium-magnesium group.

Following the classification of Alekin majority of studied ground water or fifteen samples according to the content of the anion fall within hydrocarbonate – class, three samples are in the chloride class and one sample is in the sulfate class. According to cation, content of fourteen samples include from the calcite group, five samples in the nitrite group and one sample in magnesium group.

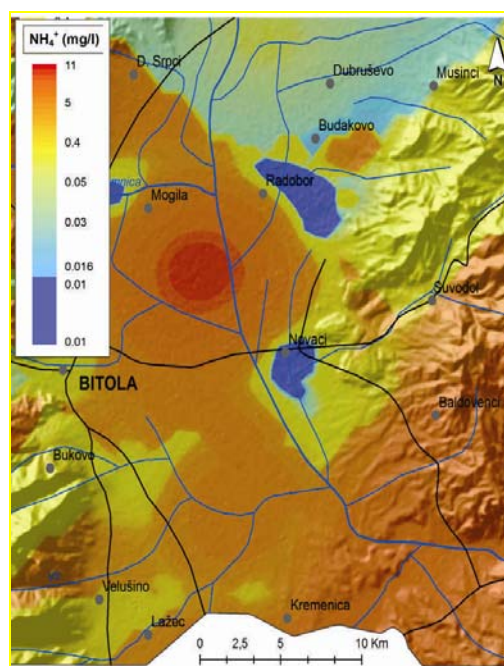


Fig. 13. Spatial distribution of NH_4^+ /mg l^{-1}

CONCLUSION

Based on the values for the content of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , NH_4^+ , NO_2^- and TDS in the ground water samples from the Bitola part of the Pelagonia valley can concluded that in the most of the tested samples were observed concentrations greater than the MPC in terms of the standard for drinking water.

Increased values of TDS, Ca_2^+ , Mg_2^+ , Na^+ , K^+ , HCO_3^- , K^+ , Cl^- and NH_4^+ occur in the ground water from deeper artesian and sub-artesian wells, as a result of the longer retention time of water in the underground and its interaction with the geological environment. Ground water from the shallow wells occurs the increasing content of

PO_4^{3-} and NO_3^- which indicates possible water pollution from fertilization of the cultivated areas, livestock farms, as well as communal waste water.

Specified values for pH indicate that the waters belong to the group of slightly alkaline ground water (pH = 7.2 – 8.9).

Following to the classification of Alekin the majority of tested water according the content of the anion fall into hydrocarbonate class, calcite group and a smaller number in the chloride and sulphate class, sodium and magnesium group (Alekin 1946).

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Резиме

ХИДРОХЕМИСКИ ПОДАТОЦИ ЗА ПОДЗЕМНИТЕ ВОДИ НА БИТОЛСКИОТ ДЕЛ ОД ПЕЛАГОНИСКАТА КОТЛИНА, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: подземни води; бунари; Пелагониска Котлина; катјони; анјони; хидрохемиски карактеристики

За определување на некои хидрохемиски податоци во подземните води на Битолскиот дел од Пелагониската Котлина, земени се еднократни примероци од 19 бунари.

Добиените вредности за рН укажуваат дека водите спаѓаат во групата на слабо алкални подземни води (рН = 7.2 – 8.9).

Според класификацијата на Alekin најголем број од испитуваните води според содржината на анјоните спаѓаат во хидрокарбонатната класа, калциска група, а помал број во хлоридната и сулфатната класа, натриумка и магнезиумка група.

Зголемување на вредностите на TDS, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- и NH_4^+ се јавува во подземните води кои потекнуваат од подлабоките артески и субартески бунари, што е резултат на подолгото време на задржување на водата во подземјето и нејзината интеракција со геолошката средина. Кај подземните води од поплитките

бунари се јавува зголемување на содржината на PO_4^{3-} и NO_3^- , што укажува на можно загадување на водите со ѓубрење на обработливите површини, од сточарски фарми, како и со комунални отпадни води.

Познавањето на хидрохемиските карактеристики на подземните води на истражуваниот простор е од посебно значење, бидејќи водата од овие бунари се користи од страна на жителите од овој регион како техничка вода, вода за наводнување, за пакување на минерална вода како и за експлоатација на CO_2 .